Supporting Information

Synthesis of 1.

A 200 mL two-necked flask, equipped with a magnetic stir bar, was charged with $[RhCl(cod)]_2$ (270 mg, 0.54 mmol, 1.5 mol%) and then flushed with argon. Cyclohexane (65 mL), P^iPr_3 (0.35 mL, 2.16 mmol, 6 mol%), Et_3N (19 mL), and HB_{pin} (3.9 mL, 27 mmol) were successively added. After being stirred at room temperature for 15 min, 3-ethynylthiophene (4.3 g, 40 mmol) was added in one-portion and the mixture was stirred at room temperature for 1.5 h before quenching by MeOH. Filtration and evaporation afforded brown oil, which was purified by bulb to bulb distillation (120 °C/1.2 Torr) to obtain product **1** as orange liquid (5.26 g, 22.1 mmol, 82%). FT-IR (neat, cm^{-1}): 2978 (s), 1614 (s), 1443 (m), 1335 (s), 1260 (s), 1144 (s), 812 (m), 673 (m). ^1H NMR (300 MHz, 25 ºC, $CDCl_3$): δ 1.32 (s, 12H), 5.47 (d, J = 15.3 Hz, 1H), 7.17 (d, J = 15.3 Hz, 1H), 7.23 (dd, J = 5.1, 2.7 Hz, 1H), 7.55-7.57 (m, 1H), 7.66 (d, J = 2.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, 25 ºC, $CDCl_3$): δ 24.9, 83.5, 124.9, 126.2, 128.6, 140.6, 141.9. MS (EI, m/z (relative intensity)): 236 (M+, 70), 178 (30), 163 (83), 151 (24), 150 (29), 137 (54), 136 (100), 135 (86), 120 (52), 111 (43). Anal. Calcd for $C_{12}H_{17}BO_2S$: C, 61.04; H, 7.26%. Found: C, 60.99; H, 7.29%.

Synthesis of 2.

A 20 mL Schlenk tube, equipped with a magnetic stirrer bar, 1,4-dichloro-2,3-diiodobenzene (40 mg, 0.1 mmol), **1** (61 mg, 0.26 mmol), PEPPSI-IPr (6.8 mg, 0.01 mmol), and KOH solid (34 mg, 0.6 mmol) were successively added. Then, 0.5 mL of toluene and 0.1 mL of H_2O were added in one-portion and the reaction mixture was stirred at 110 °C. After react for 12 h, the reaction mixture was quenched with 1 M HCl, and extracted with diethyl ether (3 × 10 mL). The combined ethereal layer was washed with brine and dried over anhydrous magnesium sulfate. Filtration and evaporation afforded brown oil, which was purified by preparative TLC (hexanes as eluent) (R_f = 0.12, hexane) to obtain product **2** as

orange liquid (17 mg, 48% yield). FT-IR (neat, cm^{-1}): 2926 (s), 1724 (s), 1634 (w), 1435 (s), 1281 (s), 1265 (m), 1125 (s), 870 (m), 797 (s), 773 (m). ^1H NMR (300 MHz, 25 ºC, $CDCl_3$): δ 6.08 (d, J = 12.0 Hz 2H), 6.56-6.60 (m, 4H), 6.91 (d, J = 2.4 Hz 2H), 7.09-7.11 (m, 2H), 7.37 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, 25 ºC, $CDCl_3$): δ 124.0, 124.3, 125.4, 126.4, 127.0, 129.4, 132.3, 137.8, 138.0. MS (EI, m/z (relative intensity)): 363 (M+, 11), 362 (15), 280 (11), 278 (16), 267 (17), 265 (25), 258 (11), 208 (14), 179 (40), 97 (100).

Synthesis of PDT-1.

A 50 mL Schlenk tube equipped with a magnetic stirring bar was charged with PCy_3 (210 mg, 0.75 mmol, 20 mol%), $PdCl_2(NCPh)_2$ (140 mg, 0.37 mmol,10 mol%), and *N*,*N*-dimethylacetamide (DMA) (8.5 mL) under argon atmosphere. After stirring for 10 min, Cs_2CO_3 (1.2 g, 3.7 mmol, 2.0 equiv), PivOH (77 mg, 0.75 mmol, 40 mol%), and substrate **2** (680 mg, 1.9 mmol) were added into reaction mixture at room temperature. The tube was put into a preheated hot box at 150 °C for 12 h. The reaction mixture was cooled to room temperature, quenched with 1 M HCl (3 mL), and extracted with chloroform (3 × 10 mL). The combined organic extracts were washed adequately by water and dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude black residue was then purified by chromatography (R_f = 0.44, hexane/$CHCl_3$ = 4/1) to afford the product (**PDT-1**, 200 mg, 38% yield) as yellowish white solid. m.p.: 242-248 °C. FT-IR (KBr, cm^{-1}): 1564 (w), 1385 (w), 1292 (s), 1088 (m), 814 (s), 802 (s), 687 (s), 590 (w). ^1H NMR (300 MHz, 25 ºC, $CDCl_3$): δ 7.56 (dd, J = 12.9, 5.4 Hz 4H), 8.06 (d, J = 9.0 Hz, 2H), 8.23 (s, 2H), 8.69 (d, J = 9.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, 25 ºC, $CDCl_3$): δ 120.4, 122.7, 123.7, 125.1, 125.8, 127.1, 127.7, 137.8, 138.9. MS (EI, m/z (relative intensity)): 290 (M+, 98), 289 (36), 258 (59), 243 (28), 209 (20), 207 (21), 145 (100), 127 (25), 99 (22), 82 (21). Anal. Calcd for $C_{18}H_{10}S_2$: C, 74.45; H, 3.47%. Found: C, 74.52; H, 3.47%.

In a similar manner, **PDT-2** was obtained in 9% yield (8.5 mg,– 0.030 mmol) as yellowish white solid from 2-ethynylthiophene as the starting material. R_f = 0.44,

hexane/$CHCl_3$ = 4/1. ^{1}H NMR (300 MHz, 25 ºC, $CDCl_3$): δ 7.66 (d, J = 5.1 Hz, 2H), 8.09-8.15 (m, 4H), 8.50 (s, 1H), 8.72 (d, J = 9.0 Hz, 2H). MS (EI, m/z (relative intensity)): 290 (M+, 100), 289 (14), 256 (8), 246 (10), 207 (35), 176 (9), 145 (23), 122 (50), 101 (8), 99 (9).